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A STUDY OF THE ELECTROLYTIC METHOD OF SILVER CLEANING.[1]

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INTRODUCTION.

An understanding of the factors which influence the tarnishing of metals and a knowledge of efficient methods for removing tarnish are necessary for the proper care of household equipment. An extended study of these problems, therefore, is being made by the Office of Home Economics, and the work reported in this paper is a part of this investigation.

The tarnishing of metals in general is due to the formation of oxids or basic oxids of the metals by the chemical action of the oxygen and water vapor of the air to which they are exposed. In the light of recent investigations a distinction is made between rusting, or oxidation, and the corrosion of metals. Thus, the rusting of iron may be regarded as taking place in two steps: The displacement of the hydrogen ions of water with the formation of a small amount of soluble iron salts in the lower state of oxidation is technically termed corrosion, while true rusting is the oxidation

[1] Prepared under the direction of C. F. Langworthy, Chief, Office of Home Economics.

Note.—This bulletin contains information regarding the advantages and limitations of the electrolytic method of cleaning silver and the conditions under which it is most efficient, which it is believed will prove useful to teachers and housekeepers generally.

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of these salts. Iron rust, then, consists principally of ferric oxid in admixture with varying amounts of basic ferric oxid. In the case of metals like copper and zinc, and alloys like brass and bronze, basic salts are also formed. For example, copper reacts with water vapor and carbon dioxid in the air to form a basic carbonate, while in the presence of weak organic acids it forms salts like basic copper acetate (verdigris).

Unlike most other metals, silver and gold are not tarnished by the oxygen, water vapor, or carbon dioxid present in the air, or by the action of weak organic acids. Silver, however, readily forms black silver sulphid on coming in contact with sulphur compounds, small quantities of which are found in the air as the result of burning coal and illuminating gas, while larger amounts occur in vulcanized rubber, wool, and foods like eggs. The problem of cleaning silver involves the removal of the tarnish of silver sulphid by some method which will also restore the polish to the surface of the metal.

The two general methods for cleaning silver are polishing with a finely divided abrasive material to cut away the tarnish mechanically and the use of suitable chemical compounds to dissolve the coating of silver sulphid. The first method is the more common one, and commercial silver polishes usually contain a suitable abrasive, such as tripoli, rouge, double-floated silica, kieselguhr, whiting, or pumice, which are prepared in the form of a powder, a cake, or a suspension in some liquid. As silver is a comparatively soft metal, and since the process of cleaning depends essentially on the cutting away of the tarnish by the sharp particles of the polishing powder, care must be taken to choose an abrasive so finely powdered that it will not scratch the silver. Solvent polishes are often used by jewelers and in hotels and restaurants where large quantities of silver must be cleaned. As a rule these consist principally of potassium cyanid and sometimes contain ammonia, both of which dissolve the sulphid coating and give the silver a beautiful satin finish. As cyanids are extremely poisonous and very dangerous when carelessly handled, they should not be commonly used for cleaning purposes.

A few years ago the so-called electrolytic method for cleaning silver was introduced to the public and several forms of cleaners, based on the electrolytic principle, are now to be found on the market. In this method the silver is cleaned by bringing it into actual contact with aluminum in a solution of an electrolyte. As this form of cleaning is becoming quite extensively used and questions are frequently asked about its efficiency and its effect on the silver, information is desirable regarding the principle and details of the process. The main object of this investigation, therefore, was to determine the value of the method and the factors necessary for its

efficient operation under household conditions. Preliminary tests were made to determine the efficiency of some representative commercial cleaners of this type and to study the nature of the metals and electrolytes commonly used.

PRELIMINARY TESTS.

The first type of electrolytic cleaner to be tested consisted of a zinc pan, on the bottom of which was fastened an aluminum grating. The directions furnished by the manufacturers for the use of this device were followed. The tarnished silver was placed on the grating and the pan filled with a dilute solution of ordinary washing soda and salt (1 teaspoonful of each to 1 quart of water) to such a height that the silver was completely covered. The liquid was kept at the boiling point until the tarnish disappeared from the silver, which was then rinsed with hot water and wiped dry. From the results of laboratory tests, in which a number of pieces of tarnished silver were cleaned by this method, it was concluded that the apparatus, although efficient, possessed no particular advantages over other less expensive methods. If a large quantity of silver is to be cleaned, however, the comparatively large capacity of the zinc pan makes the apparatus convenient. A less expensive form of this cleaner consists only of a zinc disk to the top of which are welded some aluminum wire grids. This may be used in any kettle, or in a wash boiler if large pieces of silver are to be cleaned. The silver must be placed in direct contact with the wire grids.

Still other cleaners are on the market which make use of pieces of sheet metal of various shapes. In some cases the metal alone is sold as the essential part of the "magical" method, and the instructions given with it state that the silver should be placed in contact with the metal in boiling water containing a small amount of either washing or baking soda or a mixture of one of these with common salt.

Other electrolytic cleaners consist of packages which contain a strip of metal and a powder to be dissolved in water to form the cleaning solution. Two of these were analyzed in the laboratory. The metal proved to be very pure aluminum of the spun variety, and the powder was found to consist essentially of a mixture of soda and salt.

The cleaning tests conducted in the laboratory indicated that in general tarnished silver could be cleaned equally well by all of these commercial devices. The advantages of size and convenience possessed by some seemed to correspond in every case to an increased market price, although the wide range in price makes possible the selection of a cleaner to suit a variety of conditions. These pre-

liminary experiments were of value in supplying information as to the general nature of the factors involved in the electrolytic method.

PRINCIPLE OF THE ELECTROLYTIC METHOD.

Success in using the electrolytic silver cleaners depends upon bringing the tarnished silver into actual contact with a more active metal when both are immersed in a solution of some suitable electrolyte. When so immersed aluminum and zinc are electrolytically more active than silver, or, chemically speaking, they are said to be electropositive referred to silver. In the presence of either sodium carbonate or sodium chlorid, or a mixture of both, aluminum forms aluminum ions in the solution and itself becomes negatively charged. The silver accordingly becomes positively charged as the current flows from the aluminum to the silver through the solution. In other words, such an arrangement of metals in an electrolyte may be considered to be an electrolytic cell.

Since silver sulphid is slightly soluble, a small number of silver and sulphid ions are always present in the solution, and the silver ions will give up their positive charges of electricity and plate out on the silver or negative pole as silver atoms. Any agency making the silver sulphid more soluble will increase the number of silver and sulphid ions and, provided the silver ions are plated out as rapidly as they are formed, this will increase the rate of the reaction. Moreover, in accordance with the law of mass action, the greater the number of aluminum ions formed in the solution, the greater will be the tendency for silver sulphid to be reduced to metallic silver. The conditions are apparently most favorable to the completion of the reaction when a dilute solution of sodium carbonate is used as the electrolyte. The hydrolysis of this salt furnishes a fairly strong alkaline solution.

(1) $$Na_2CO_3+2H_2O \rightarrow H_2O+CO_2+2NaOH.$$

Aluminum then displaces hydrogen from a boiling solution of the alkali.

(2) $$Al+3NaOH \rightarrow Na_3AlO_3+3H.$$

The atomic hydrogen supplied by this reaction reduces the silver sulphid.

(3) $$Ag_2S+2H \rightarrow H_2S+2Ag.$$

When an excess of hydrogen ions is continually being formed, the sulphid ions are gradually removed to form molecules of H_2S. In this way the equilibrium between Ag_2S (undissociated) and its ions is disturbed, and accordingly more Ag_2S dissolves. The reaction finally is completed and, since the excess of aluminum ions plates out the silver on the silver pole, practically no silver is lost.

EXPERIMENTAL STUDY OF THE METHOD.

It was the chief purpose of these experiments to obtain information as to the best metal and electrolyte to use, the most economical concentration of the solution, and the most satisfactory temperature for cleaning silver as it would ordinarily be accomplished in the home, and to study the relative efficiency of the electrolytic and other methods.

Throughout the investigation the methods and apparatus were simple and in most cases applicable to household use, more accurate procedure being deemed impracticable. In some cases silver which had been naturally tarnished by use was cleaned satisfactorily by this method, but in order to secure uniform conditions the silver used in most tests was tarnished by immersing it in a strong potassium-sulphid solution, and in order that the tarnish should be uniform for a comparative series of tests, all of the spoons to be used in each series were placed in the sulphid solution for the same length of time. Porcelain or agate ware dishes were used for holding the solution of electrolyte, which was made up by adding different amounts of soda and salt, etc., to one or two quarts of water. The active metal used, aluminum, or zinc, or an alloy of both, and the tarnished silver were then placed in direct contact in the solution which had previously been heated to the desired temperature, and the time necessary for cleaning was noted by a stop watch.

Since the preliminary tests indicated that either washing or baking soda may be used as the electrolyte of the cleaning solution, it seemed desirable to ascertain first of all whether either of these salts was the more efficient and economical for ordinary household use. Experiments were accordingly made to determine the relative efficiency of solutions of washing soda and baking soda without the addition of sodium chlorid. The concentration of the solutions was 1 teaspoonful of the commercial soda to 1 quart of water. The temperature at which the cleaning was done was approximately 100° C. in each case. In each series six spoons were used which had been tarnished as described above. The following procedure was adopted: The first spoon was cleaned in the washing-soda solution. The active metal was then rinsed in clean water, transferred to the baking-soda solution, and another spoon cleaned. By alternating from one solution to the other in this way, any error in the time of cleaning, resulting from the metal becoming corroded, was distributed equally between the two solutions. After removal from the cleaning solution the spoons were rinsed in cold water and wiped thoroughly dry with a soft cloth, rubbing very slightly.

Table I shows the results of the tests:

TABLE I.—*Comparative efficiency of solutions of washing and baking soda at the boiling temperature.*

Solution.	Time required for cleaning.		Remarks.
	Observed.	Average.	
Series 1.	*Seconds.*	*Seconds.*	
Washing soda	30		
Do	10	16	Zinc was the active metal used in series 1, 2, and 3.
Do	7		
Baking soda	10		
Do	10	10	
Do	11		
Series 2.			
Washing soda	240	.....	
Do	20	18	The exceptionally long time required in the first test of series 2 and 3 was due to the zinc becoming corroded; it was necessary to substitute a strip of clean zinc before the tarnish was removed. In such cases the time has been disregarded in computing the average.
Do	15		
Baking soda	17		
Do	10	12	
Do	9		
Series 3.			
Washing soda	150	.....	
Do	10	8	
Do	5		
Baking soda	27		
Do	4	13	
Do	8		
Series 4.			
Washing soda	5		
Do	7	10	Aluminum was the active metal used in series 4 to 9, inclusive.
Do	18		
Baking soda	6		
Do	10	15	
Do	28		
Series 5.			
Washing soda	10		
Do	12	11	
Do	10		
Baking soda	13.5		
Do	9	11	
Do	11		
Series 6.			
Washing soda	20	20	
Baking soda	30	30	
Series 7.			
Washing soda	5		
Do	4.5	4	In series 7 and 8 a small sheet of very pure aluminum of the spun variety was used.
Do	2		
Baking soda	7		
Do	7.5	6	
Do	4.5		
Series 8.			
Washing soda	8		
Do	12	10	
Do	10		
Baking soda	7.5		
Do	7	7	
Do	7		

TABLE I.—*Comparative efficiency of solutions of washing and baking soda at the boiling temperature*—Continued.

Solution.	Time required for cleaning.		Remarks.
	Observed.	Average.	
Series 9.			
	Seconds.	*Seconds.*	
Washing soda	5		
Do	4	4	The aluminum used in series 9 had been cleaned by polishing with emery cloth.
Do	2.5		
Baking soda	4		
Do	4	4	
Do	5.5		
Series 10.			
Washing soda	4		
Do	3	3	In series 10, 11, and 12 the active metal used was zinc. In series 10 it was cleaned after each test in dilute HCl and rinsed in water.
Do	2		
Baking soda	2		
Do	3	3	
Do	3		
Series 11.			
Washing soda	5		
Do	4	5	The zinc was not cleaned with acid in series 11.
Do	5		
Baking soda	3		
Do	3.5	4	
Do	4.5		
Series 12.			
Washing soda	3		
Do	5	5	The zinc had been standing in the hot cleaning solution for 10 minutes before use in series 12 and was not cleaned with acid.
Do	6		
Baking soda	5		
Do	7	8	
Do	11		

From the results of these experiments it is evident that washing soda is slightly more efficient than baking soda, the average time required, considering all of the tests, being 9½ seconds for the washing-soda solution and 10½ seconds for the baking-soda solution. For all practical purposes, since the difference between the efficiency of washing soda and that of baking soda is so small as to be within the limits of experimental error, it may be considered feasible to use them interchangeably. As far as the appearance of the cleaned spoons was concerned, no difference was noted in the two solutions; all the spoons that were cleaned showed a bright satin finish after each cleaning and were practically as bright at the end of each experiment as at the start. Washing soda is somewhat more economical, since it is more efficient and cheaper as well.

The next factor to be considered was the effect of increasing the conductivity of the cleaning solution, and common salt was used for this purpose. In the following experiments the silver to be cleaned was uniformly tarnished by immersing the spoons in the same tarnishing solution for the same length of time. In some of the tests alu-

minum was the active metal, in others zinc was used, and in a few cases an alloy, which was prepared in the laboratory by melting together zinc and aluminum. Two cleaning solutions were used: One contained 1 teaspoonful of washing soda per quart of water, and the other was made up of 1 teaspoonful each of washing soda and salt to every quart of water. The results obtained are given in Table II.

TABLE II.—*The effect of varying the concentration of the electrolyte by the addition of sodium chlorid.*

Solution.	Time required for cleaning.		Remarks.
	Observed.	Average.	
Series 13.	*Seconds.*	*Seconds.*	
Washing soda	3		
Do	5	4	Aluminium was the active metal used in series 13.
Do	3		
Washing soda+salt	2		
Do	1	1	
Do	1		
Series 14.			
Washing soda	10		
Do	4	7	In series 14, 15, and 16 zinc was the active metal, which was cleaned frequently with dilute HCl.
Do	6		
Washing soda+salt	3		
Do	3	3	
Do	3		
Series 15.			
Washing soda	3		
Do	2.5	3	
Do	2.5		
Washing soda+salt	1.5		
Do	1	1	
Do	1		
Series 16.			
Washing soda	3		
Do	2.5	3	
Do	3		
Washing soda+salt	2.5		
Do	1	2	
Do	2		
Series 17.			
Washing soda	160		
Do	15	15	The alloy of zinc and aluminum was used in series 17. The exceptionally long time observed in two instances was necessary to clean two parts of the same silver buckle, badly tarnished by use.
Do	15		
Washing soda+salt	140		
Do	12	11	
Do	10		

The data recorded in Table II indicate that the average time required for cleaning the silver was less when sodium chlorid was added to the solution. For all practical purposes, however, the difference is so slight as to be of little or no consequence. It is reasonable to assume that by increasing the concentration of the electrolyte, as is the case when sodium chlorid is added, the cleaning reaction will take place somewhat more rapidly. This conclusion is strengthened by further experiments carried out to study the effect of the concen-

tration of the solution on the rate of cleaning. It was found, for example, that with a solution of one-tenth teaspoonful of washing soda to 1 quart of water the time of cleaning was approximately six times as long as when 1 teaspoonful was used. Conversely, the increase in the rate of the reaction when concentrations of the electrolyte as high as 1 tablespoonful to 1 quart of water were used was not sufficient to warrant the use in practice of larger amounts than 1 teaspoonful.

As a result of these tests it is believed that a teaspoonful of sodium carbonate to 1 quart of water, with or without the addition of about 1 teaspoonful of sodium chlorid, is the most satisfactory concentration of the cleaning solution for general use.

RELATIVE EFFICIENCY OF ZINC AND ALUMINUM.

A study of the tables with reference to the time required for cleaning the silver with aluminum and with zinc indicates that in general there is little difference in the efficiency of these metals. In some instances aluminum and in others zinc cleaned the silver more rapidly. This apparent inconsistency is probably due to the fact that in some cases the metals became corroded or that the tarnish in some series of tests was slightly heavier than in others. Although the zinc cleaned very efficiently when first put into the solution, it soon became corroded and its efficiency thereby greatly reduced. For example, in three tests it was found that spoons having a uniform tarnish were not cleaned at the end of four, five, and four minutes, respectively, by a piece of zinc which had become corroded. After a new piece of zinc was substituted the spoons were cleaned in as many seconds. After the corroded zinc had been cleaned by immersing for about one minute in a solution of hydrochloric acid (one part HCl sp. gr. 1.2 to 10 parts of water) it cleaned practically as well as the new metal. Attempts were made to restore the efficiency to the corroded zinc by cleaning it with vinegar and also by rubbing it with various abrasives such as sand soap and emery paper, but without success.

EFFECT OF TEMPERATURE OF CLEANING SOLUTION.

A few experiments were made to determine whether this method of cleaning is efficient below boiling temperatures, since under household conditions it might be desirable to clean very large pieces of silver, which could be boiled only with difficulty, by immersing them in the hot cleaning solution contained in a tub or bucket. It was found, on an average, that at temperatures as low as 40° C. the silver was cleaned only after being immersed several minutes; at temperatures from 50 to 60° C. in about ten seconds; and at temperatures from 60 to 100° C. in about five seconds. At temperatures much be-

low the boiling point, although the tarnish was removed, the cleaned silver had a somewhat dull appearance. From the results of these tests it is evident that the cleaning solution should be kept at the boiling point, since the tarnish is more quickly removed and the silver has a much brighter appearance than when cleaned in cooler solutions. In cases where it is not possible to boil the articles to be cleaned very hot cleaning solutions can be used with fairly satisfactory results.

RELATIVE MERITS OF THE ELECTROLYTIC AND POLISHING METHODS OF CLEANING SILVER.

From the theory of the cleaning process as formulated earlier in the paper it would appear that there is practically no loss in weight of the silver cleaned by the electrolytic method, since the tarnish of silver sulphid is merely reduced to metallic silver. In order to verify this, however, three sterling silver and three silver-plated spoons were weighed, tarnished and cleaned 50 times, and weighed after the final cleaning, zinc being used in a solution of 1 teaspoonful of sodium carbonate in 1 quart of water at the boiling temperature. During the 50 cleanings the three sterling silver spoons lost 0.0043, 0.0034, and 0.0034 grams and the three plated spoons lost 0.0026, 0.0019, and 0.0024 grams, or an average of 0.00006 grams in each cleaning. This loss is insignificant when compared with the loss in polishing with an abrasive silver polish which actually cuts away the tarnish, as was shown by the following test. One sterling silver and one silver-plated spoon were weighed, tarnished and cleaned six times by rubbing with a paste of finely powdered whiting and water, and weighed after the last cleaning. The spoons lost 0.0094 and 0.0087 grams, respectively, or an average of 0.0015 grams in each cleaning, about 25 times as much as by the electrolytic method. For a further comparison three sterling silver spoons were weighed, tarnished, and cleaned six times with a 5 per cent solution of potassium cyanid. By this method the spoons lost in weight 0.0135, 0.0129, and 0.0123 grams, respectively, an average of 0.0022 grams in each cleaning, a greater loss than by either of the other methods.

While the electrolytic method removes the tarnish effectively and with practically no loss of metal, it gives the articles cleaned a satin finish rather than the bright burnished appearance obtained when abrasive polishes are used. After the spoons used in these experiments had been cleaned a number of times by the electrolytic method it was found necessary to rub them with the paste of whiting and water to restore their original bright polish. In practice, therefore, it may be found desirable to use the electrolytic method as frequently as is necessary to remove the tarnish and to rub the silver with some

good abrasive polish only as often as may be desirable to restore the burnished appearance.

A combination of the two methods is sometimes used by adding one or two teaspoonfuls of finely powdered whiting to each quart of the cleaning solution, and after removal the silver is allowed to dry without being rinsed. The film of whiting which adheres to it is then rubbed off with a soft cloth. This has the advantage of convenience, but the polish obtained is not so bright as when the two methods are used separately.

After one has tried both methods of cleaning silver it is obvious that much less labor is involved in the use of the electrolytic than the polishing method. As sodium carbonate in the form of washing soda and table salt are to be found in most homes, and since a small piece of aluminum or zinc can be purchased for a few cents, the cost of the two methods need not differ very much.

A HOUSEHOLD METHOD.

The details of a satisfactory method for household use are essentially as follows: An enamel or agate ware dish should be partly filled with a cleaning solution of 1 teaspoonful of either washing or baking soda and 1 teaspoonful of common table salt to each quart of water and placed directly on the stove to boil. A sheet of aluminum or clean zinc should then be dropped into the dish and the tarnished silver placed in contact with this metal. It is best that the silver be entirely covered with the cleaning solution and that the solution remain at the boiling temperature. As soon as the tarnish has been removed the silver should be removed, rinsed in clean water, and wiped with a soft cloth.

Aluminum corrodes quickly in the cleaning solution, so that aluminum dishes of any value for culinary purposes should never be used. Aluminum ware, which would otherwise be thrown away, or any inexpensive piece of the metal, will serve very satisfactorily for cleaning silver. Zinc may be used in place of aluminum, but it becomes corroded and inactive in a much shorter time. Unless it is possible to obtain a strong acid, such as muriatic acid, in which the activity of the zinc may be frequently renewed, it is inadvisable to try to employ this metal in the electrolytic method for cleaning silver.

SUMMARY.

Experiments have shown that the commercial devices for cleaning silver by the action of aluminum in solutions of soda are generally satisfactory. Zinc is less satisfactory than aluminum because it

becomes corroded and loses its efficiency. Sodium carbonate or bicarbonate, with or without the addition of sodium chlorid, are equally effective as the electrolyte of the solution, although to secure the best results the solution during cleaning should be kept at the boiling temperature. The electrolytic method cleans plated or sterling silverware without loss of metal, giving, however, a satin finish rather than a burnished appearance, and has the additional advantages of being clean and labor-saving.

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